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(71) Applicant: Chisso Corporation
6-32, Nakanoshima 3-chome Kita-ku
Osaka-shi Osaka-fu(JP)

(72) Inventor: Nakano, Takaharu
523, Kubiri 2-chome
Yokosukashi Kanagawaken(JP)

(72) Inventor: Ohtake, Nobumasa
10-2, Otsutomocho Kanazawaku
Yokohamashi Kanagawaken(JP)

(74) Representative: Lamb, John Baxter et al,
Marks & Clerk 57/60 Lincoln's Inn Fields
London WC2A 3LS(GB)

(54) Carboxyl group-containing siloxane compounds.

(57) Carboxyl group-containing siloxane compounds have the formula:

$$R-\left(\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-O\right)_{\ell}\left(\underset{R^2}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-O\right)_m-\underset{R^1}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-R \qquad (I)$$

in which R is a C_1C_4 alkyl group; R^1 is a group R or a group R^2; R^2 is a group $CH_2CH_2CH_2(OCH_2CH_2)_nCOOH$ (in which n is an integer of 1 or more); ℓ is 0 or an integar of 1 or more; m is 0 or an integar of 1 or more; $\ell+m$ is an integer of 1 or more; and R^1 is a group R^2 when m is 0.

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CARBOXYL GROUP-CONTAINING SILOXANE COMPOUNDS

This invention relates to carboxyl group-containing siloxane compounds.

In general, carboxyl group-containing siloxane compounds are useful for a number of applications where, for example, organosiloxane compounds soluble in water or alcohols are desired. Thus, for example, carboxyl group-containing siloxane compounds may be used as emulsifying agents for forming aqueous emulsions of organosiloxane polymers or may be used in alcohol-based cosmetics. Further, carboxy group-containing siloxane compounds may be expected to have strong adhesion onto inorganic materials and to modify the surface of the materials so as to impart to the surface functions such as water repellency, stain resistance, non-adhesive properties, heat resistance, abrasion resistance, etc. For example, as disclosed in Japanese laid-open patent applications Nos. Sho 53-10882/1978 or Sho 57-10145/1982, such siloxane compounds have been used as an ink-repelling material for litho printing.

In a conventional carboxyl group-containing siloxane compound the carboxyl group is linked to the compound by a group of the formula:

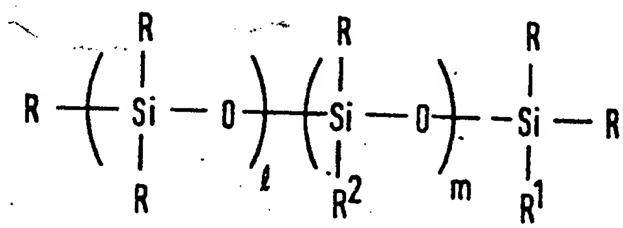
$$-\overset{|}{\underset{|}{Si}}-\!\left(CH_2\right)_s\!-COOH$$

wherein s is 2, 3 or 4, as described, for example, in Japanese patent publications Nos. Sho 40-20279/1965, Sho 41-236/1966, Sho 42-6519/1967 and Sho 49-4840/1974. We have found that such conventional carboxyl group-containing siloxane compounds are stable to heat when they have a number average molecular weight (Mn) greater than 1,000, but are decomposed by heat when Mn is 1,000 or less.

We have further found that when a carboxyl group is bonded to the compound via a difunctional group containing a polyoxyethylene chain, the resultant compounds are stable to heat even if they are of low molecular weight.

The object of the present invention is, thus, to provide a carboxyl group-containing siloxane compound, whether of low or high molecular weight, having a superior heat stability and which may be used as an emulsifying agent, a surface modifier for inorganic materials, etc.

According to the invention there is provided a carboxyl group-containing siloxane compound of the formula



(I)

in which R is a C_1-C_4 alkyl group; R^1 is a group R or a group R^2; R^2 is a group $-CH_2CH_2CH_2-(OCH_2CH_2)_n$ COOH (in which <u>n</u> is an integer of 1 or more); ℓ is 0 or an integer of 1 or more; <u>m</u> is 0 or an integer of 1 or more; ℓ+m is an integer of 1 or more; and R^1 is a group R^2 when <u>m</u> is zero.

In the above general formula, $\underline{n}$ has no particular upper limit and may be e.g. several thousands or several tens of thousands. The $\underline{m}$ and $\underline{\ell}$ also each have no particular upper limit and may be e.g. several millions or several tens of millions.

The difference in behaviour between the compounds of the inventions and conventional carboxyl group-containing siloxane compounds is illustrated by the fact that a compound of the formula:

$$Me_3SiO\overset{\displaystyle Me}{\underset{\displaystyle Me}{\overset{|}{\underset{|}{Si}}}}CH_2CH_2CH_2COOH \qquad (II)$$

(in which Me is a methyl group) undergoes a ring closure reaction at about 150°C to give a product of unknown structure, whereas a compound of the formula

$$\mathrm{Me_3SiOSi(Me)_2CH_2CH_2CH_2OCH_2CH_2COOH} \qquad \text{(III)}$$

(which is in principle the compound of formula (II) containing an added ethyleneoxy group) is sufficiently stable to permit of distillation at 150°C/1 mm Hg.

The carboxyl group-containing compounds of the invention may be prepared by subjecting an ester of the formula:

$$\mathrm{CH_2=CHCH_2 \left(OCH_2CH_2 \right)_n COOR^3}$$

(in which R^3 is, for example, a methyl, ethyl or trimethylsilyl group) and an Si-H-containing siloxane compound to hydrosilylation and subsequently hydrolysing the resulting ester.

The esters of formula (IV) compound in which _n_ is 1 and R^3 is methyl or ethyl can be easily obtained by subjecting allyl alcohol to an addition reaction with acrylonitrile in the presence of a basic catalyst [see Ind. Eng. Chem., 44, 2867 (1952)], followed by alcoholysis of the nitrile group of the resulting product. When methanol is used as a solvent in the alcoholysis, the methyl ester can be obtained, while when ethanol is used, the ethyl ester can be obtained [see Org. Synth., 1, 270 (1941)]. Further, when the esters obtained by the above reactions are further hydrolyzed in the presence of a basic catalyst to obtain the corresponding carboxylic acid, followed by reaction this acid with hexamethyldisilazane, it is possibile to obtain the trimethylsilyl ester [see J. Org. Chem., 40, 1610 (1975)].

Esters of formula (IV) in which _n_ is 2 or more can be prepared in a similar manner using in place of the allyl alcohol, a compound of the formula:

$$CH_2 = CHCH_2 \left(OCH_2CH_2 \right)_n OH \qquad (V)$$

which may be prepared by the addition reaction of the necessary number of mols of ethylene oxide with allyl alcohol.

A specific class of carboxyl group-containing siloxane compounds of the invention are those of the formula:

$$\mathrm{Me_3SiO}\left(\underset{\underset{\displaystyle Me}{|}}{\overset{\overset{\displaystyle Me}{|}}{\mathrm{Si}}}\mathrm{O}\right)_r\underset{\underset{\displaystyle Me}{|}}{\overset{\overset{\displaystyle Me}{|}}{\mathrm{Si}}}\mathrm{-CH_2CH_2CH_2OCH_2CH_2COOH} \qquad (VI)$$

wherein r represents 0 or an integer of 1 or more.

The compound (VI) may be readily obtained from (a), when r id 0, a readily commercially available siloxane compound containing a hydrogen atom at one end or (b) when r is 1 or more, siloxane compounds containing a hydrogen atom at one end obtained by reacting lithium trimethylsiloxanolate with hexamethylcyclotrisiloxane to give a siloxane compound containing H atom at its one end [see Polym. Preprints, 10 (2), 1361 (1969)], and then subjecting these to addition reaction with an ester of formula (IV) in which R^3 is a trimethylsilyl group in the presence of a catalyst for addition reaction,

preferably under a nitrogen gas atmosphere, followed by subjecting the resulting product to detrimethyl-silylation with an alcohol.

As to the siloxane compound containing an H atom at one end, it is possible to optionally prepare a siloxane compound having a controlled molecular weight and molecular weight distribution, as far as its average molecular weight is about 10,000 or lower. In the reaction of the siloxane compound having an H atom at one end which the trimethylsilyl ester, the ester is suitably used an at least equimolecular quantity to the siloxane compound, preferably in an amount of 1.2 moles per mole of siloxane compound. The reaction temperature is suitably to from 40 to 200°C, preferably from 80 to 130°C. Suitable catalysts for the addition reaction are complex compounds of metals of group 8 of the Periodic Table may be exemplified, e.g. platinum compounds, rhodium compounds or palladium compounds such as known alcohol compounds, aldehyde compounds or the like of chloroplatinic acid, complexes of chloroplatinic acid with various olefins, etc.

The alcohol used for detrimethylsilylation is preferably methanol or ethanol.

The following carboxyl group-containing siloxane compounds (VII) and (VIII) can be easily prepared by similarly reacting the corresponding SiH-containing compound with the trimethylsilyl ester.

$$HOOCCH_2CH_2O(CH_2)_3\overset{Me}{\underset{Me}{Si}}O-\left(\overset{Me}{\underset{Me}{Si}}O\right)_t-\overset{Me}{\underset{Me}{Si}}(CH_2)_3OCH_2CH_2COOH \qquad (VII)$$

wherein t is 0 or an integer of 1 or more.

$$Me-\left(\overset{Me}{\underset{Me}{Si}}O\right)_{l}-\left(\overset{Me}{\underset{(CH_2)_3OCH_2CH_2COOH}{Si}}O\right)_{m}-SiMe_3 \qquad (VIII)$$

(In case of this example m is an integer of 1 or more.)

The compounds of the invention are useful for various applications, for example as emulsifying agents for forming aqueous emulsions of organosiloxane polymers, as ingredients for alcohol-based cosmetics, or as a surface modifier for imparting to the surface of inorganic materials, functions such as water repellency, stain resistance, non-adhesive properties, heat resistance, abrasion resistance, etc.

In order that the invention may be well understood the following examples are given by way of illustration only.

Reference example

(1) Allyl alcohol (150 g, 2.58 mols) and an ion exchange resin (IRA-400, trade name of a strongly basic anion exchange resin made by Rohm & Haas Company, U.S.A.) (25 g) were fed into a flask in N_2 current and the temperature was kept at 45°C, followed by dropwise adding acrylonitrile (125 g, 2.35 mols) over about 1 to 2 hours, thereafter agitating the mixture at 45°C for about 8 to 9 hours, filtering off the resin and carrying out vacuum distrillation to obtain cyanoethyl allyl ether (196 g, 93 ~ 96°C/20 mmHg). Yield: 75%.

(2) Ethanol (350 mℓ), water (34.4 mℓ) and conc. sulfuric acid (200 mℓ) were fed into a flask, followed by dropwise adding cyanoethyl allyl ether (222 g, 2 mols) at room temperature over 30 minutes, thereafter agitating the mixture at a reaction temperature of 100 ~ 110°C for about 7 hours, pouring the reaction fluid into water, extracting it with isopropyl ether, washing the extract solution with 5% $NaHCO_3$ aqueous solution till the extract solution became neutral, drying over $MgSO_4$, and subjecting the extract solution to vacuum distillation to obtain 2-allyloxypropionic acid ethyl ester (147.2 g, 94°C/18 mmHg). Yield: 46%.

(3) 2-Allyloxypropionic acid ethyl ester (147.2 g, 0.93 mol), water (300 mℓ) and NaOH (44.7 g) were fed

into a flask, followed by agitating the mixture for about 5 to 6 hours while the reaction temperature was kept at about 60°C, thereafter dropwise adding conc. hydrochloric acid (90 mℓ) under ice cooling, extracting the resulting deposited oily substance with isopropyl ether, drying over $MgSO_4$ and carrying out vacuum distillation to obtain 2-allyloxypropionic acid (95.7 g, 108°C/5 mmHg). Yield: 79%.

The thus obtained 2-allyloxypropionic acid (170.2 g, 1.31 mol) was fed into a flask, followed by dropwise adding hexamethyldisiloxane (128.8 g, 0.8 mol) in N_2 current at room temperature over one hour, thereafter raising the reaction temperature to 80°C, then agitating the mixture for about 3 hours, and carrying out vacuum distillation to obtain 2-allyloxypropionic acid trimethylsilyl ester (3c) (231.4 g). Yield: 87.5%.

Example 1

2-Allyloxypropionic acid trimethylsilyl ester (65.5 g, 0.32 mol) obtained in the above Reference example, and a solution of chloroplatinic acid in isopropanol (0.042 mol; chloroplatinic acid 1 g/20 mℓ) were fed into a flask in N_2 current, followed by raising the temperature to 100°C, thereafter dropwise adding pentamethyldisiloxane (40 g, 0.27 mol) with stirring over 30 minutes, then further carrying out reaction at 100°C for 2 hours, and subjecting the resulting reaction mixture solution to vacuum

distillation to obtain a colorless, transparent liquid having a b.p. of 120°C/1 mmHg (77.9 g, yield 82.4%). This product was confirmed to be a silicon compound having the following structural formula, from the following analytical results:

$$\begin{array}{c} Me \\ | \\ Me-Si \\ | \\ Me \end{array} O- \begin{array}{c} Me \\ | \\ Si \\ | \\ Me \end{array} -(CH_2)_3OCH_2CH_2COO- \begin{array}{c} Me \\ | \\ Si \\ | \\ Me \end{array} -Me$$

H−NMR(C_2H_4):

δ 0.06 (Si−CH_3, s, 15H)

0.3 (−CO_2SiMe_3, s, 9H)

0.56 (−CH_2−Si, m, 2H)

1.56 (−CH_2−, m, 2H)

2.5 (−CH_2−, t, 2H, J = 6Hz)

33 (−CH_2−, t, 2H, J = 6Hz)

3.6 (−CH_2−, t, 2H, J = 6Hz)

IR(KBr):

νmax 2960 cm^{-1} (C−H)

1740 cm^{-1} (C=O)

1120∼1050 cm^{-1} (Si−O)

MSm/e: 350 (M^+)

Next, the thus obtained compound (77.9 g, 0.23 mol) and methanol (100 mℓ) were fed into a flask, followed by agitating the mixture at room temperature for about 2 ~ 3 hours and subjecting the resulting reaction fluid to vacuum distillation to obtain a colorless, transparent liquid having a b.p. of 150°C/1 mmHg (61 g, yield: quantitative). This product was confirmed to be an oxyethylenecarboxylic acid-modified compound having the following structural formula, from the following analytical results.

$$\mathrm{Me}-\underset{\displaystyle\mathrm{Me}}{\overset{\displaystyle\mathrm{Me}}{\underset{|}{\overset{|}{\mathrm{Si}}}}}\ \mathrm{O}-\underset{\displaystyle\mathrm{Me}}{\overset{\displaystyle\mathrm{Me}}{\underset{|}{\overset{|}{\mathrm{Si}}}}}-(CH_2)_3OCH_2CH_2COOH$$

H−NMR(C_2Cl_4):

δ 0.06 (Si−CH_3, s, 15H)

0.56 (−CH_2−Si, m, 2H)

1.6 (−CH_2−, m, 2H)

2.5 (−CH_2−, t, 2H, J = 6 Hz)

3.3 (−CH_2−, t, 2H, J = 6 Hz)

3.6 (−CH_2−, t, 2H, J = 6 Hz)

11.6 (−CO_2H, s, 1H)

IR(KBr): ν max 3050 (CO_2H)

2960 cm^{-1} (C−H)

1740 cm^{-1} (C=O)

1120~1050 cm^{-1} (Si−O)

MSm/e: 278 (M^+)

This product was stable without causing any ring closure reaction in the vicinity of 150°C.

Example 2

2-Allyloxypropionic acid trimethyl ester (40.2 g, 0.2 mol) was reacted with a siloxane polymer containing H atom at both the ends thereof ($\bar{M}n$ 1,100, H equivalent 547) in the same manner as in Example 1, followed by distilling off unreacted raw materials and a low boiling substance from the reaction mixture fluid under a reduced pressure (150°C/1 mmHg) for 2 hours, and washing the residual fluid with water till the residual fluid became neutral to obtain a colorless, transparent liquid (111.6 g). This product was confirmed to be an oxyethylene-carboxylic acid-modified silicone having the following structural formula, from the following analytical results:

$$HOOCCH_2CH_2O(CH_2)_3 \left(\begin{matrix} Me \\ | \\ SiO \\ | \\ Me \end{matrix} \right)_p \begin{matrix} Me \\ | \\ Si \\ | \\ Me \end{matrix} -(CH_2)_3OCH_2CH_2COOH$$

IR(KBr): νmax 3100 (CO_2H)

3000~2950 (C–H)

1740 (C=O)

1125~1060 (Si–O)

Carboxylic acid equivalent: 672 (theoretical value 677)

$\bar{M}n$: 1344 (calculated from carboxylic acid equivalent)

Side chain signals were confirmed according to H-NMR:

δ 0.56 ($-CH_2-Si$, m, 2H)

1.6 ($-CH_2-$, m, 2H)

2.5 ($-CH_2-$, t, 2H, J = 6 Hz)

3.3 ($-CH_2-$, t, 2H, J = 6 Hz)

3.3 ($-CH_2-$, t, 2H, J = 6 Hz)

Example 3

Reaction was carried out in the same manner as in Example 2 except that the above siloxane polymer containing H atom at both the ends thereof was replaced by a siloxane polymer containing pendant type H atom (41.9 g, $\bar{M}n$ 5300, H equivalent 252) to obtain a colorless, transparent liquid (61.6 g). This product was confirmed to be an oxyethylenecarboxylic acid-modified silicone having the following structural formula, from the following analytical results:

$$Me-\left(\begin{array}{c}Me\\ |\\ SiO\\ |\\ Me\end{array}\right)_{\ell}-\left(\begin{array}{c}Me\\ |\\ SiO\\ |\\ (CH_2)_3OCH_2CH_2COOH\end{array}\right)_{m}-SiMe_3$$

IR(KBr) : ν max 3110 (CO_2H)

3000～2950 (C–H)

1740 (C=O)

1125～1050 (Si–O)

Carboxylic acid equivalent: 390 (theoretical value 382)

$\bar{M}n$: ≃ 7800 (calculated from GPC)

$\bar{\ell}$: ≈ 55, $\bar{m}$: ≈ 20 (calculated from GPC, H equivalent and infrared absorption spectra)

Side chain signals were confirmed accordin to H-NMR:

δ 0.56 ($-CH_2-Si$, m, 2H)

1.6 ($-CH_2-$, m, 2H)

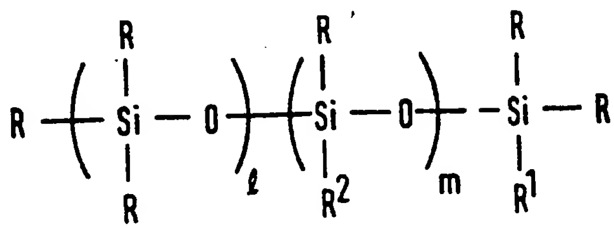
2.5 ($-CH_2-$, t, 2H, J = 6 Hz)

3.3 ($-CH_2-$, t, 2H, J = 6 Hz)

3.3 ($-CH_2-$, t, 2H, J = 6 Hz)

Claims

1. A carboxyl group-containing siloxane compound of the formula



(I)

in which R is a C_1-C_4 alkyl group; R^1 is a group R or group R^2; R^2 is a group $-CH_2CH_2CH_2(OCH_2CH_2)_n COOH$ (in which *n* is 0 or an integer of 1 or more); *ℓ* is 0 or an integer of 1 or more; *m* is 0 or an integer of 1 or more; ℓ+m is an integer of 1 or more; and R^1 is a group R^2 when *m* is 0.

2. A compound according to claim 1 characterised in that *m* is ten million or less.

3. A compound according to claim 2 characterised in that *m* is one million or less.

4. A compound according to any one of the preceding claims characterised in that *ℓ* is ten million or less.

5. A compound according to claim 4 characterised in that $\underline{l}$ is one million or less.

6. A compound according to any one of the preceding claims characterised in that $\underline{n}$ is 10,000 or less.

7. A compound according to claim 6 characterised in that $\underline{n}$ is 1,000 or less.

8. A compound according to claim 1 characterised in that it has a number average molecular weight of 7,8000 or less.

9. A compounds according to claim 8 characterised in that it has a number average molecular weight of 1,000 or less.

$$-\overset{|}{\underset{|}{Si}}-\!\left(CH_2\right)_s-COOH$$

$$R-\left(\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O\right)_{\ell}-\left(\overset{R}{\underset{R^2}{\overset{|}{\underset{|}{Si}}}}-O\right)_m-\overset{R}{\underset{R^1}{\overset{|}{\underset{|}{Si}}}}-R \qquad (I)$$

$$Me_3SiO\overset{Me}{\underset{Me}{\overset{|}{\underset{|}{Si}}}}CH_2CH_2CH_2COOH \qquad (II)$$

$$Me_3SiO\overset{Me}{\underset{Me}{\overset{|}{\underset{|}{Si}}}}CH_2CH_2CH_2OCH_2CH_2COOH \qquad (III)$$

$$CH_2=CHCH_2-\left(OCH_2CH_2\right)_n-COOR^3 \qquad (IV)$$

$$CH_2=CHCH_2-\left(OCH_2CH_2\right)_n-OH \qquad (V)$$

$$Me_3SiO\left(\begin{array}{c}Me\\ |\\ SiO\\ |\\ Me\end{array}\right)_r\begin{array}{c}Me\\ |\\ Si\\ |\\ Me\end{array}\!-CH_2CH_2CH_2OCH_2CH_2COOH \qquad (VI)$$

$$HOOCCH_2CH_2O(CH_2)_3\begin{array}{c}Me\\ |\\ SiO\\ |\\ Me\end{array}\!-\!\left(\begin{array}{c}Me\\ |\\ SiO\\ |\\ Me\end{array}\right)_t\!-\!\begin{array}{c}Me\\ |\\ Si\\ |\\ Me\end{array}(CH_2)_3OCH_2CH_2COOH$$

(VII)

$$Me-\left(\begin{array}{c}Me\\ |\\ SiO\\ |\\ Me\end{array}\right)_{\ell}-\left(\begin{array}{c}Me\\ |\\ SiO\\ |\\ (CH_2)_3OCH_2CH_2COOH\end{array}\right)_m-SiMe_3 \qquad (VIII)$$